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THE VELOCITY OF HYDROLYSIS OF ETHYL ACETATE

BY

ROBERT PFANSTIEL

A THESIS

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

IN CHEMISTRY

The Collegiate Press
GEORGE BANTA PUBLISHING COMPANY
MENASHA, WIS.
1922

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As a result of considerable evidence, Mac Innes (Jour. Amer. Chem. Soc. 41, 1086 [1919]) has arrived at the conclusion that in solutions of the same molality of hydrochloric acid, lithium, sodium, and potassium chlorides, the chlorine ion has the same activity. He further made the assumption that in a solution of a given strength, the activities of the potassium and chlorine ions are the same. These hypotheses received considerable confirmation in dilute solutions from the electromotive force measurements of Ming Chow (Jour. Amer. Chem. Soc. 42, 477 [1920]) and in concentrated solutions by Harned (Jour. Amer. Chem. Soc. 42, 1808 [1920]). On the basis of these assumptions, Harned calculated from existing electromotive force data the individual ion activity coefficients of these uni-univalent electrolytes. If Mac Innes' assumptions are correct it follows from these calculations that the activity coefficient of the hydrogen ion in dilute solutions of hydrochloric acid decreases until a concentration of 0.15 M. is reached and then increases quite rapidly. In any event, this activity coefficient must exhibit a minimum in the neighborhood of from 0.1 M. to 0.2 M. concentration.

These conclusions, if true, or valid within narrow limits, will be of considerable importance in the calculation of equilibria in solutions as well as homogeneous catalysis. Consequently, this investigation was undertaken with the purpose of finding out whether further support for the above hypothesis could be obtained from a study of hydrogen ion catalysis.

It has been found that the monomolecular velocity constant of hydrolysis of ethyl acetate in dilute solutions of hydrochloric acid is roughly proportional to the concentration of the acid. It was first thought that the velocity of hydrolysis was proportional to the hydrogen ion concentration, but it was soon found that the velocity constant increased with increasing acid concentration more rapidly than the hydrogen ion concentrations as computed from the conductance or conductance viscosity ratios. To explain this, Senter

(Trans. Chem. Soc., 91, 467 [1907]), Acree (Amer. Chem. Jour., 37, 410, and 38, 258 [1907]), Taylor (Meddel. K. Vetensk. Nobelinst., 2, No. 37 [1913]), and others have proposed the theory that the undissociated acid molecule, as well as the hydrogen ion, exerts a catalytic effect. In contradistinction to this, another theory has been proposed which relates the reaction velocity to the ion activities as defined by G. N. Lewis (Proc. Amer. Acad. Arts Sci. 43, 259 [1907]; Jour. Amer. Chem. Soc., 35, 1 [1913], etc.). Lewis has shown that in a chemical equilibrium the exact thermodynamic expression for the law of mass action of a general reaction such as

$$aA+bB+\ \ldots\ \rightleftharpoons dD+eE+\ \ldots\ \text{ is}$$

$$K=\frac{a_{\mathrm{D}}^{\mathrm{d}}\cdot a_{\mathrm{E}}^{\mathrm{e}}}{a_{\mathrm{A}}^{\mathrm{a}}\cdot a_{\mathrm{B}}^{\mathrm{b}}} \qquad (1)$$

where a_A, a_B, etc., represent the activities of the species A, B, etc., respectively, and K is an equilibrium constant. Thus, if the equilibrium is a dynamic one, the velocity from left to right and the velocity from right to left will be given respectively by

$$\begin{aligned} v_1&=k_1\ a_{\mathrm{A}}^{\mathrm{a}}\cdot a_{\mathrm{B}}^{\mathrm{b}} \\ v_2&=k_2\ a_{\mathrm{D}}^{\mathrm{d}}\cdot a_{\mathrm{E}}^{\mathrm{e}} \end{aligned} \qquad (2)$$

If the velocities depend on successive states of equilibria, and no interfering factors such as contact surfaces, light radiation, etc., are present, the above equations for the velocities are a thermodynamic necessity.

At the present time the mechanism of ester hydrolysis is not well known. The theory which has the most evidence in its favor is the one which assumes the formation of an intermediate compound (Stieglitz—Congress of Arts and Sciences—St. Louis 4, 276 [1904]). Here the reaction takes place in two steps. The first is a rapid reaction between the ester, hydrogen ion, and water, to form the intermediate compound, and the second is a slow decomposition of the intermediate compound producing the alcohol and acid, and regenerating the hydrogen ion. Thus

$$CH_3COOC_2H_5+H_2O+H^+\rightleftharpoons\left[CH_3C\begin{array}{l}\ulcorner O\text{-}H\\ \llcorner O\text{-}H\end{array}\!\!-O-C_2H_5\right]^+ \qquad (a)$$

(H bridging the two O-H groups)

and

$$\left[CH_3C\begin{array}{l}\ulcorner O\text{-}H\\ \llcorner O\text{-}H\end{array}\!\!-O-C_2H_5\right]^+\rightleftharpoons CH_3COOH+C_2H_5OH+H^+ \qquad (b)$$

(H bridging the two O-H groups)

The equilibrium of reaction (a) is represented by

$$K = \frac{a_i}{a_e \cdot a_H \cdot a_w}$$

where a_i, a_e, a_H, and a_w are the activities of the intermediate compound, ester, hydrogen ion, and water species. The velocity of the reaction from left to right will be given by

$$v_1 = k a_i$$

Hence

$$v_1 = k_1 \, a_e \cdot a_H \cdot a_w \quad \ldots\ldots (3)$$

Throughout this paper k_1 will represent the velocity from left to right.

Since by definition $F_e \cdot c$ equals a_e, where F_e is the activity coefficient of the ester and c is its concentration, substitution in (3) gives

$$v_1 = k_1 (F_e \cdot c) \cdot a_H \cdot a_w \quad \ldots\ldots (4)$$

At a given temperature k_1 remains constant under changing conditions of all other factors in equation (4)

Let $k'_1 = k_1 \cdot a_H \cdot a_w$;

Then $$\frac{k'_1}{a_H \cdot a_w} = k_1 \quad \ldots\ldots (4a)$$

Substituting the value of k'_1, in (4) gives

$$v_1 = k'_1 \cdot (F_e \cdot c) \quad \ldots\ldots (4b)$$

From (4a), k'_1 is proportional to a_H and a_w. During the course of reaction in a given experiment a_H and a_w remain constant and k'_1 therefore represents the velocity constant in each experiment. Since the velocity constant is obtained by measurement of c, equation (4b) shows that $k'_1 F_e$ instead of k'_1 is obtained. Therefore in the Tables to follow $k'_1 F_e$ will always represent the velocity constant. Equation (4a) shows that $\frac{k'_1 F_e}{a_H \cdot a_w}$ will not remain constant if F_e vary. F_e will vary if the solubility of the ester changes with changing hydrochloric acid concentration because F_e is a function of the solubility. This can be seen from the following thermodynamic reasoning: The activity of the ester in a saturated solution in the presence of the liquid ester at the same pressure and temperature will always have the same value. Therefore, if a', a'', a''', etc., represent the activities of the ester in varying acid concentrations, and C', C'', C''' etc., represent the concentrations of the ester in the saturated solutions,

Then $a' = a'' = a''' = \text{etc.}$

$$\text{or } \frac{a'}{C'}C' = \frac{a''}{C''}C'' = \frac{a'''}{C'''}C''' = \text{etc.}$$

$$\text{or } F_e'C' = F_e''C'' = F_e'''C''' = \text{etc.}$$

Substituting S', S'', S''', etc., or the solubilities for the contentrations in the saturated solutions gives

$$F_e'S' = F_e''S'' = F_e'''S''' = F_eS = \text{constant} \ldots\ldots\ldots\ldots (5)$$

From (4a) and (5) is obtained

$$\frac{k_1' F_e}{a_H \cdot a_w} \cdot S = k_1 (F_e S) = \text{constant} \ldots\ldots\ldots\ldots\ldots\ldots (5a)$$

Earlier work on this subject is not sufficient to prove the validity of equation (5a). A compilation of previous data taken from the work of Taylor (Meddel. K. Vetensk. Nobelinst., 2, No. 37, [1913]), Kay (Proc. Royal Soc. Edinb., 22, 484 [1897]) and Lunden (Zeit. Phy. Chem., 49, 189 [1904]) on the hydrolysis of ethyl acetate and other esters is contained in a paper by Schreiner (Zeit. anorg. chem., 116, 102, [1921]). These results are reproduced in Table I.

TABLE I

Ethyl Acetate Hydrolysis

Hydrochloric acid Concentration c	$(k'_1 \cdot F_e) \cdot 10^5$	$\frac{(k'_1 \cdot F_e) \cdot 10^5}{c}$
0.010	2.93	293.
0.025	6.99	280.
0.050	13.83	278.
0.100	28.29	283.
0.132	38.10	288.
0.150	43.20	288.
0.200	57.00	285.
0.250	71.60	286.
0.479	138.00	288.
0.493	145.00	296.

Thus, the velocity constant divided by the concentration passes through a minimum at about 0.05 M. hydrochloric acid. This is similar to the behavior of the activity coefficient of the hydrogen ion as mentioned above. This evidence is by no means conclusive, but is suggestive due to the parallelism between these properties. Consequently, further careful work has been undertaken in order to clear up, if possible, some of the difficulties.

I. EXPERIMENTAL

The experimental method employed throughout in determining the velocity constants is the same as that usually employed, namely,

titration from time to time of the total acid present in the ester-hydrochloric acid mixture by means of sodium and barium hydroxide solutions. Densities of all the solutions were determined so that the calculations could be made on either a weight or a volume normal basis. Further, all solutions were so standardized that it was possible to compute the absolute quantities of all the molecular species present at any time during the course of the reaction. Since calculations were made by both the monomolecular formula and by the general kinetic formula for the reaction, it will be necessary to discuss the procedure in some detail.

(a) MATERIALS

Ethyl acetate was prepared from alcohol and acetic acid, and purified in the usual way. After repeated fractional distillation, the portion which passed over between 77° and 78° was collected for the investigation. Analysis of this fraction gave 98.81% saponifiable ester, free from acetic acid. Tests for free acetic acid were made from time to time during the course of the investigation and in no case was it found present.

Constant boiling hydrochloric acid was diluted to 3M, and checked by gravimetric analysis. All solutions of the acid were made from this sample by the weight method and were correct to within 0.1% of the total hydrochloric acid content. Conductivity water freed from carbon dioxide by boiling was employed.

The sodium hydroxide and barium hydroxide solutions used to titrate the total acid (hydrochloric, and acetic formed during the hydrolysis of the ester) were kept in carbon dioxide free bottles. The sodium hydroxide solutions were freed from carbonate by the addition of small quantities of barium hydroxide.

All flasks used were cleaned with a sulphuric-chromic acid mixture, followed by the introduction of a jet of steam. After drying, they were provided with paraffined cork stoppers.

(b) METHOD OF PROCEDURE

Each determination was carried out in a ¼ liter flask. In all the determinations 200 grams of water were employed. The molal concentration of the hydrochloric acid (mols of hydrochloric acid in 1000 grams of water) varied from 0.01 to 1.5. In a given series the same quantity of ethyl acetate was added to each flask. Thus in every determination of a given series the same quantity of water and the

same quantity of ester was employed, the only variable being the hydrochloric acid content. Two series of results were obtained using 5 c.c. and 1 c.c. of ester to 100 grams of water.

In every determination, the quantity of hydrochloric acid solution necessary for a given molal concentration of hydrochloric acid in 200 grams of water was calculated, and then weighed in a small weighing bottle, care being taken to avoid loss by evaporation while weighing. It was then washed into a previously weighed 250 c.c. flask. Water was then added until the weight obtained was equal to the weight of the flask, the HCl, and 200 grams of water. The flask was then placed in a thermostat in which a temperature of $25° \pm 0.01$ was maintained. After the contents of the flask had acquired the same temperature as the bath, ethyl acetate at 25° was added to the solution from a pipette. Two series of experiments were conducted, differing from one another only in the ester concentration. In the one series 10 c.c., and in the other 2 c.c. of ethyl acetate were added to each solution. In each case, the quantity of ester added was determined by taking the average weight of several pipetted portions of ethyl acetate, the same conditions as to temperature and delivery of pipette being observed.

The addition of as much as 10 c.c. of ester caused a noticeable rise in temperature, amounting to 1° in cases where the molal concentration of hydrochloric acid was 0.5 or higher. Therefore before pipetting for the initial titration, it was necessary to wait until the temperature was reduced to 25°.

As soon as all the ester was dissolved and the liquid had assumed the temperature of the bath, a 10 c.c. portion was withdrawn with a pipette and delivered into a beaker containing a little water and some phenolphthalein. While the pipette was delivering, sodium hydroxide from a burette was introduced at a rate sufficient to neutralize the hydrochloric acid in the hydrolyzing solution as fast as it was discharged from the pipette. Since the time of the initial titration and all subsequent titrations were noted the time always taken was the instant when the pipette was half discharged. From eight to ten titrations were made in each determination at successive time intervals during the course of the reaction. A 0.04426 N. barium hydroxide solution was employed in all cases as titrating agent, and for solutions containing the higher hydrochloric acid concentrations a stronger solution of sodium hydroxide was also used. In the latter case, the initial titrations were made with the stronger alkali, and

the subsequent titrations were made by first adding the same amount of sodium hydroxide as was used in the initial titration and then completing the determination by the addition of barium hydroxide.

(c) KINETICS OF THE REACTION

In what follows, a very careful study has been made of the velocity constants calculated by both the simplified and approximate monomolecular reaction equation, and the more general kinetic equation which takes into consideration the reverse reaction.

(1) The Kinetics of the First Order Reaction.

The general equation for the kinetics of the reaction, $RCOOR' + H_2O \leftrightarrows RCOOH + R'OH$, in going from left to right and assuming that the activities of the four molecular species are proportional to their concentrations and that the hydrogen ion activity remains constant, will be

$$\frac{dx}{dt} = {}^*k_1'' (A-x)(B-x) - k_2x^2 \quad \ldots\ldots\ldots\ldots\ldots (6)$$

where $\frac{dx}{dt}$ is the velocity, A and B the initial concentrations of ester and water, x the amount of ester changed in the time, t, and k_1'' and k_2 are the velocity constants of hydrolysis and esterification respectively. Since the water concentration, B, varies only slightly during the reaction, and since the reaction goes nearly to completion when a relatively large quantity of water is present, equation (6) may be reduced to the simpler and approximate monomolecular equation

$$\frac{dx}{dt} = k_1''(A-X) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

which upon integration takes the well known form

$$k_1'' = \frac{1}{t} ln \frac{A}{A-X} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

This equation when expressed in terms of the titers becomes

$$k_1'' = \frac{1}{t} ln \frac{T_\infty - T_0}{T_\infty - T} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

where T_∞ is a number slightly greater† than the final titer, T_0 the initial titer, and T the titer at any time t.

* $k_1'' = (k_1'Fe)$.

† Explained later.

(2) The General Kinetic Equation.

In equation (6), namely, $\frac{dx}{dt}=k_1''\ (A-x)\ (B-x)-k_2x^2$, k_1'' and k^2 are both unknowns. Therefore k_2 must be eliminated.

Let $\frac{dx}{dt}=0=k_1''\ (A-x)\ (B-x)-k_2x^2$,

then $\frac{k_2}{k_1''}=\frac{(A-x)\ (B-x)}{x^2}=K$ (equilibrium constant)

and $k_2=k_1''\cdot K$ .....(10)

K can be determined experimentally since $\frac{dx}{dt}=0$ represents the end point in a titration.

(Subst. for k_2 in [6]) $\frac{dx}{dt}=k_1''\ (A-x)\ (B-x)-k_1''\ Kx^2$.....(11)

or $$\frac{dx}{dt}=k_1''\ \{x^2-(A+B)x+AB\}-k_1''\ Kx^2$$

or $$\frac{dx}{dt}=k_1''\ (1-K)\left(x^2-\frac{A+B}{1-K}x+\frac{AB}{1-K}\right)$$

$$\frac{dx}{x^2-\frac{A+B}{1-K}x+\frac{A\cdot B}{1-K}}=k_1''\ (1-K)\ dt \qquad .....(12)$$

$$\int\frac{dx}{x^2-\frac{A+B}{1-K}x+\frac{A\cdot B}{1-K}}=k_1''\ (1-K)t+C \qquad .....(13)$$

To integrate the expression on the left hand side of equation (13), let

$$\alpha+\beta=\frac{A+B}{1-K} \qquad .....(14)$$

and $$\alpha\cdot\beta\ =\frac{A\cdot B}{1-K} \qquad .....(15)$$

Then $$\int \frac{dx}{x^2-\frac{A+B}{1-K}x+\frac{A\cdot B}{1-K}} = \int \frac{dx}{x^2-(a+\beta)x+a\cdot\beta} =$$

$$= \int \frac{dx}{(a-x)\ (\beta-x)} = \int \frac{dx}{(\beta-a)\ (a-x)} - \int \frac{}{(\beta-a)\ (\beta-x)} =$$

$$= \frac{1}{\beta-a} ln\ (\beta-x) - \frac{1}{\beta-a} ln\ (a-x) =$$

$$= \frac{1}{\beta-a} ln\ \frac{\beta-x}{a-x} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

Equation (13) becomes $\frac{1}{\beta-a}\ ln\ \frac{\beta-x}{a-x} = k_1''\ (1-k)t+C$ ..... (17)

To evaluate the constant C, let $t=o$, then $x=o$, and

$$C = \frac{1}{\beta-a}\ ln\ \frac{\beta}{a}$$

Subst. value of C in (17): $\frac{1}{\beta-a}\ ln\ \frac{a(\beta-x)}{\beta(a-x)} = k_1''(1-K)t$ ..... (18)

$$k_1'' = \frac{2.3026}{(1-K)\ (\beta-a)t} \log \frac{a(\beta-x)}{B\ (a-x)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (19)$$

For substituting back in equation (19) the values of a and β, in terms of A, B, and K, equations (14) and (15) must be solved simultaneously.

$$a = \frac{A+B+\sqrt{(A+B)^2-4\ A\cdot B\ (1-K)}}{2\ (1-K)}$$

$$\beta = \frac{A+B-\sqrt{(A+B)^2-4\ A\cdot B\ (1-K)}}{2\ (1-K)}$$

$$k_1'' = \frac{2.3026}{t\sqrt{(A+B)^2-4\ A\cdot B\ (1-K)}}\ \log \left\{ \frac{A+B-\sqrt{(A+B)^2-4\ AB(1-K)}}{A+B+\sqrt{(A+B)^2-4\ AB(1-K)}} \cdot \right.$$

$$\left. \frac{A+B+\sqrt{(A+B)^2-4\ AB\ (1-K)}-2\ (1-K)x}{A+B-\sqrt{(A+B)^2-4\ AB\ (1-K)}-2\ (1-K)x} \right\} \ldots\ldots (20)$$

Equation (20) is reduced to a simpler form by letting

$$l=\frac{2.3026}{\sqrt{(A+B)^2-4AB\ (1-K)}},\quad m=\frac{A+B-\sqrt{(A+B)^2-4\ A\cdot B(1-K)}}{A+B+\sqrt{(A+B)^2-4A\cdot B(1-K)}}$$

$$\times 2\ (1-K),\ \text{and}\ n=A+B-\sqrt{(A+B)^2-4\ A\cdot B\ (1-K)}.$$

By substitution in (20)

$$k_1''=\frac{l}{t}\log\left(\frac{n-mx}{n-2\ (1-K)x}\right)\ldots\ldots\ldots\ldots\ldots(21)$$

Griffith and W. C. McC. Lewis, (Jour. Chem. Soc., 109, 67 [1916]) indicate how equation (6) may be integrated by a different substitution. Knoblauch (Zeit. für Physk. Chemie 22, 268, [1897]) integrated a similar equation by a different substitution.

(D) CALCULATION, AND TABLES OF VELOCITY CONSTANTS COMPUTED FROM MONOMOLECULAR EQUATION

In computing k_1'' according to the monomolecular equation (9), T_∞ represents the quantity of alkali which would be required for titration after complete hydrolysis. Since the reaction does not go to completion, T_∞ cannot be determined experimentally. Therefore T_∞ was calculated in each experiment as follows: The weight of 10 c.c. of the solution, delivered from the pipette used in each titration, was determined. Let this be "a." In the preparation of the solutions the weight of each component was known. Let b equal the weight of the water, d the weight of hydrochloric acid, and e the weight of the ester in the reaction flask. Then $\frac{a}{b+d+e}\cdot d$ is the number of grams of hydrochloric acid, and $\frac{a}{b+d+e}\cdot e$ is the number of grams of ethyl acetate (assuming no hydrolysis), in each pipette. Therefore, the alkali equivalent of both the hydrochloric acid and the ethyl acetate in cubic centimeters, or T_∞ is readily obtained. It is important to note that employing this value for T_∞ gave lower values for the velocity constants than would have been obtained by taking for T_∞ the titration value at equilibrium. Although the velocity constants show a greater variation in value (due to the influence of the reverse raction) as the reaction approaches equilibrium, than is apparent when the final titration value for T_∞ is taken for calculating the results, the values of the velocity constants

at the beginning of the reaction are more consistent. For the above reason the values for k_1'' will be lower than other values given in the literature. In Table II the results of an average experiment, calculated by the above method, are compared with the results obtained by using the titer value for T_∞. T_∞ = calculated value, and T'_∞ = titer value.

TABLE II

Temp. = 25°c. 0.15 M. HCl

	$T_\infty - T_0 = 97.52$		$T'_\infty - T_0 = 94.55$	
Time Minutes	$T_\infty - T$	$(k_1' F_e) \cdot 10^4$	$T'_\infty - T$	$(k_1' F_e) \cdot 10^4$
157	84.52	9.112	81.55	9.402
281	75.49	9.112	72.52	9.440
421	66.27	9.176	63.30	9.526
526	60.39	9.110	57.42	9.480
736	49.92	9.098	46.95	9.502
1148	34.55	9.039	31.58	9.552
1455	26.57	8.934	23.60	9.536
1829	19.42	8.823	16.45	9.560
2091	15.77	8.713	12.80	9.562
2966	8.59	8.190	5.62	9.519

The velocity constants for the different acid concentrations are given in Table III. They are the mean of the constants for the first half of the reaction which in all cases gave concordant results. The constants for two series, differing in the concentration of the ester employed, are given. In each series two determinations of the velocity constants for each acid concentration were made and the mean value recorded. $k_1' F_e$ is the mean velocity constant, C_1 is the molal concentration of hydrochloric acid, and C_2 is the normal concentration of hydrochloric acid.

(e) CALCULATIONS OF THE EQUILIBRIUM CONSTANT

In the calculation of the velocity constant by the general equation, it is necessary to employ a value for the equilibrium constant. The classic work of Berthelot and St. Gilles gives the value of 4. Knoblauch, (Zeit. physik. Chem., 22, 268 [1897]) using an equimolecular mixture of alcohol and water, a high concentration of ester, and hydrochloric acid as a catalyst, obtained 2.67. Jones and

TABLE III

C_1	C_2	$(k_1'F_e)\cdot 10^5$	$\frac{(k_1'F_e)\cdot 10^5}{C_1}$	$\frac{(k_1'F_e)\cdot 10^5}{C_2}$
		0.470 N. Ester		
0.01	0.00952	6.11	611	642
0.03	0.02857	18.30	610	641
0.05	0.04759	30.00	600	630
0.07	0.06666	41.79	597	627
0.10	0.09510	60.15	601	632
0.15	0.1425	91.10	607	639
0.20	0.1900	122.2	611	643
0.30	0.2840	185.5	618	653
0.50	0.4726	312.4	625	661
0.70	0.6604	450.0	643	681
1.00	0.9354	640.0	640	684
1.50	0.1391	1006.	671	723
		0.100 N. Ester		
0.01	0.00987	6.37	637	645
0.03	0.02961	18.96	632	640
0.05	0.0493	31.74	634	644
0.07	0.0690	44.44	635	644
0.10	0.0985	63.56	636	645
0.15	0.1477	95.54	637	647
0.20	0.1966	129.0	645	656
0.30	0.2944	197.2	657	670

Lapworth (Trans. Chem. Soc., 99, 1427 [1911]) found that in the presence of large quantities of hydrochloric acid the equilibrium constant was somewhat greater than 4. With methyl acetate, at a concentration of 1.15 to 1.74 normal, Griffith and Lewis (Jour. Chem. Soc. 109, 67 [1916]) obtained for K, in the presence of $N/2$ hydrochloric acid, 4.30, 4.52, 4.66, and 4.80. Since no definite information regarding the value of K for the hydrolysis of ethyl acetate in the presence of hydrochloric acid of concentrations here employed could be obtained, the equilibrium constant was determined at each acid concentration. Great accuracy could not be obtained on account of the experimental conditions. The large concentration of water forces the reaction to within 3% of completion, thus magnifying the errors of the determination. However, when the results in Table IV are compared with those of Griffith and Lewis who employed an ester concentration four times greater than that employed in this investigation, the concordance of values must be considered excellent, and a good confirmation of the accuracy of this work.

TABLE IV

$$K=\frac{(A-x)\ (B-x)}{x_2}$$

C_1	A	X	B	K
0.01	0.4737	0.4600	52.85	3.39
0.03	0.4737	0.4582	52.85	3.87
0.05	0.4737	0.4596	52.85	3.50
0.07	0.4737	0.4581	52.85	3.89
0.10	0.4731	0.4576	52.79	3.87
0.15	0.4728	0.4583	52.74	3.61
0.20	0.4727	0.4567	52.73	4.01
0.30	0.4713	0.4554	52.63	4.00
0.50	0.4701	0.4545	52.45	3.93
0.70	0.4679	0.4533	52.20	3.68
1.00	0.4652	0.4519	51.91	3.35
			Mean	3.74

Since there is no apparent increase or decrease of the equilibrium constant within the limits of these hydrochloric acid concentrations, and since the mean value checks, within the present experimental error, the value of Berthelot and St. Gilles, the value of 4 for the equilibrium constant has been employed in all subsequent calculations.

(f) METHOD OF CALCULATION, AND TABLES OF VELOCITY CONSTANTS OF HYDROLYSIS COMPUTED FROM THE GENERAL EQUATION

Substituting the value of 4 for K in equation (21), the final form for the general kinetic equation is

$$k_1''=\frac{l}{t}\log\frac{n-mx}{n-6x} \qquad (22)$$

In order to employ this equation it is necessary to obtain the values of A, the initial concentration of ester; B, the initial concentration of water; and x, the concentration of the ester changed in a time t. A and B were readily obtained since the weight of the ester and water, and the density of the solutions were known. Their calculation needs no explanation. Therefore, it remains only to show how x is calculated and how a slight change is made in T_0 and in the first reading of t. From equation (22) when t equals 0, x must equal zero. Under the experimental conditions, it is impossible to start the experiment at the beginning of the hydrolysis. When the first titra-

tion is made, some ester has hydrolyzed, and x therefore has an appreciable value when t equals 0. Therefore T_0, the initial titration, is corrected to a value which will give x equal 0, and t is corrected so as to make the beginning of the time the moment when x equals °. The following consideration will explain how this correction is made: Let the initial titration be T_0. Calculate T_∞. Then the ester equivalent, T_e, of the contents of one pipette of the solution in terms of cubic centimeters of alkali is calculated. Then $T_\infty - T_e = T'_0$. T'_0 is less than T_0 by a quantity of alkali equivalent to the acetic acid formed from the beginning of hydrolysis up to the time of the first titration. Now the lapse of time from the beginning of hydrolysis up to the time of the first titration may be computed from the equation:

$$t = \frac{2.302}{k} \log \frac{T_\infty - T'_0}{T_\infty - T_0} \qquad (23)$$

This time is added to the time period of each successive titration. The value of x for each titration will be $\frac{T - T'_0}{T_e} \cdot A = x$. Table V gives a comparison of the velocity constant as obtained from the first order and second order equations.

TABLE V

$c_1 = 0.20$ $c_2 = 0.1897$

Equation (9)			Equation (22)			
(1) Time Minutes	(2) $T - T_0$	(3) $(k_1'F_e)$	(4) Time Minutes	(5) $T - T_0'$	(6) x(mols)	(7) $(k_1'F_e)\cdot 10^5$
			48	6.03	0.02675	
71	8.47	0.001240	119	14.50	0.06433	2.340
158	17.82	0.001236	206	23.85	0.1058	2.345
259	27.48	0.001234	307	33.51	0.1486	2.345
371	36.71	0.001226	419	42.74	0.1895	2.337
491	45.42	0.001226	539	51.45	0.2283	2.347
638	54.30	0.001218	686	60.33	0.2676	2.335
837	63.90	0.001208	885	69.93	0.3102	2.338
1010	70.75	0.001206	1058	76.78	0.3406	2.353
	97.00[i]			103.03[r]	0.4570[x']	
	100.45[j]			106.48[v]	0.4724 A	

i = end point r = end point x' = equilibrium value of x.
j = $T_\infty - T_0$ v = $T_\infty - T'_0 = T_e$ A = initial conc. of ester.

From the Table it is seen that the time of hydrolysis began 48 minutes before the first titration was made, and in that time enough acetic acid was formed to neutralize 6.03 cc. of alkali. The time in column (4) was obtained by adding 48 to the figures in column (1), and the values in column (5) were obtained by adding 6.03 to the figures in column (2).

Equation (22) gave constant values for k_1'' when calculated from the titrations near the equilibrium point of the reaction. In Table VI is compiled the mean values of k_1'' obtained by equation (22). c_1 is molal concentration, and c_2 is normal concentration of the hydrochloric acid. $(k_1'F_e)$ equals k_1''.

TABLE VI

c_1	c_2	$(k_1'F_e)\cdot 10^6$	$\frac{(k_1'F_e)\cdot 10^6}{c_1}$	$\frac{(k_1'F_e)\cdot 10^6}{c_2}$
		0.47 N. Ester		
0.01	0.00952	1.167	116.7	122.6
0.03	0.02857	3.442	114.7	120.5
0.05	0.04759	5.729	114.5	120.4
0.07	0.06666	7.971	113.9	119.6
0.10	0.0951	11.46	114.6	120.5
0.15	0.1425	17.36	115.8	121.8
0.20	0.1900	23.27	116.3	122.5
0.30	0.2840	35.34	117.8	124.5
0.50	0.4726	60.05	120.1	127.1
0.70	0.6604	86.03	122.9	127.3
1.00	0.9354	125.2	125.2	133.8
1.50	1.391	196.1	130.8	141.0
		0.100 N. Ester		
0.01	0.00987	1.166	116.6	118.2
0.03	0.02961	3.450	115.0	116.5
0.05	0.0493	5.782	115.6	117.3
0.07	0.0690	8.094	115.6	117.3
0.10	0.0985	11.55	115.5	117.3
0.15	0.1477	17.57	117.1	119.0
0.20	0.19660	23.65	118.3	120.3
0.30	0.2944	35.95	119.8	122.1

Table VI shows that in the first series corresponding to an initial ester concentration of 0.47 normal the values obtained for the ratios of the velocity constants to the hydrochloric acid normalities are greater than they are in the second series, corresponding to an initial ester concentration of 0.100 normal. If the activity of the hydrogen ion is not changed by increasing the ester concentration

and there is no other catalytic influence, then according to the general kinetic equation a change in ester concentration at constant hydrochloric acid normality should not affect the velocity constant. However, this difference is in agreement with the results of Griffith and Lewis (Jour. Chem. Soc. 109, 67 [1916]) who, working at constant volume and at constant hydrochloric acid concentration, found that the velocity constant increased with increasing ester concentration. They ascribed the cause to a negative catalytic effect of the water.

II. Discussion

The hydrolysis of a comparatively simple substance as ethyl acetate may be regarded as a type reaction for all hydrolytic reactions. Consequently, a solution of the kinetics and mechanism of this reaction is a problem of very great importance. However, the phenomenon of the simplest case of hydrolysis is extremely complex because so many ionic and molecular species are involved. To obtain a complete solution of its kinetics requires a knowledge of the concentrations and activities of all the species at any time during the course of the reaction.

The position which is taken in this investigation is based on thermodynamic reasoning, and ascribes all the catalytic effect of the acid to the hydrogen ion. An inspection of Tables I, III, and VI show that in each case the ratio of the velocity constant to the concentration of the hydrochloric acid gives a minimum value somewhere between 0.05 and 0.10 normal concentration of hydrochloric acid. There can be no possible doubt that this minimum exists, since besides being supported by the work of others it was verified in every instance in the present investigation. The theory of catalytic activity of undissociated hydrochloric acid molecules fails to explain this minimum.

As mentioned in the introduction, if it be assumed that the potassium ion has the same activity as the chlorine ion in a solution of given strength of potassium chloride, and if it also be assumed that in solutions of the same strength of hydrochloric acid and potassium chloride, the chlorine ion activity is the same, then it follows that the hydrogen ion activity coefficient passes through a minimum in the neighborhood of from 0.1 to 0.2 molal concentration of hydrochloric acid, and then rises rapidly. Employing these assumptions, which have considerable evidence for their support,

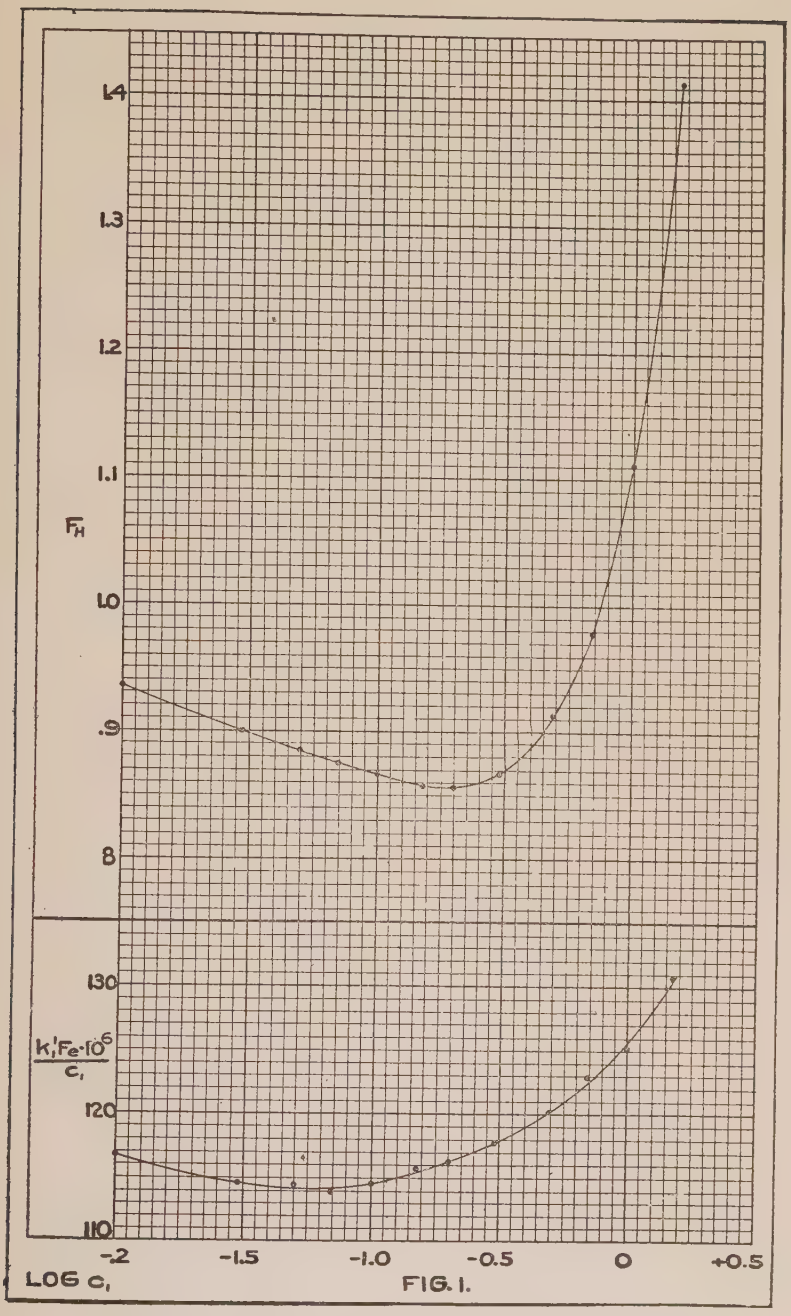
1.4
1.3
1.2
1.1
F_H
1.0
.9
.8
130
$\frac{k_1' Fe \cdot 10^6}{c_1}$
120
110
-2
-1.5
-1.0
-0.5
0
+0.5
LOG c_1

FIG. 1.

Harned (loc. cit.) has computed the independent hydrogen activity in hydrochloric acid solutions from the electromotive force data of Ellis (Jour. Amer. Chem. Soc. 38, 737 [1916]) and Noyes and Mac Innes (ibid. 42, 239 [1920]). The hydrogen ion activity coefficient from these results is given by

$$\log F_H = 0.330\, c - 0.284\, c^{0.471}$$

(Harned—Jour. Amer. Chem. Soc. 44, 252 [1922]), where F_H is activity coefficient of the hydrogen ion.

In Fig. I are given plots of $\frac{k_1' F_e}{c_1}$ (Table VI) against log c_1 and also F_H against log c_1. It is clear that with increasing acid concentration the value of the ordinate first passes through a minimum and then rises rapidly in both cases. The minimum of each curve occurs between 0.07 and 0.20 molal concentration of hydrochloric acid. However, in dilute solutions F_H decreases more rapidly than $\frac{k_1' F_e}{c_1}$, while in concentrated solutions it increases more rapidly. Therefore if the values of $k_1' F_e$ are divided by the activity of the hydrogen ion a constant is not obtained. This is illustrated in Table VII. In column

TABLE VII

(1) c_1	(2) F_H	(3) a_w*	(4) $\frac{(k'F_e)\cdot 10^6}{a_H}$	(5) $\frac{(k'F_e)\cdot 10^6}{a_H \cdot a_w}$
0.01	0.935		1.248	1.248
0.03	0.903		1.270	1.270
0.05	0.886		1.292	1.293
0.07	0.875		1.302	1.303
0.10	0.868	0.997	1.320	1.324
0.15	0.858	0.995	1.350	1.357
0.20	0.857	0.993	1.357	1.367
0.30	0.867	0.990	1.359	1.373
0.50	0.914	0.983	1.314	1.337
0.70	0.979	0.975	1.255	1.287
1.00	1.112	0.964	1.126	1.168
1.50	1.416	0.942	0.924	0.980

*Calculated from the vapor pressure of water over hydrochloric acid solutions (Harned—loc. cit.)

(1) are molal concentrations of hydrochloric acid, and in column (2) are the corresponding activity coefficients of the hydrogen ion; column (3) contains the activity of the water molecule for the

various acid concentrations; column (4) gives the ratios of the velocity constants (computed from the general kinetic equation, Table VI) to the corresponding hydrogen ion activities; and column (5) contains the ratios of the velocity constant to the product of the hydrogen ion and water activities.

It is seen from the Table that the values of $\frac{(k_1'F_e)}{a_H}$ and $\frac{(k_1'F_e)}{a_H \cdot a_w}$ are not constant, but have a maximum at 0.3 M. acid concentration. This is not due to experimental error. In the more concentrated solutions, it is possible that the deviation is due to an error in calculating the hydrogen ion activity which may have a lower value than the calculated one. On the other hand, as already pointed out, $\frac{(k_1'F_e)}{a_H \cdot a_w}$ should not be a constant if F_e varies with the acid concentration. The value of F_e in solutions of hydrochloric acid can be obtained theoretically from either the measurement of the partial vapor of the ester above the solution, or from the solubility. It was shown that $\frac{k_1'F_e}{a_H \cdot a_w} S$ should be constant. Consequently, if the solubility decreases with increasing acid concentration the correction for F_e will be in the right direction. A determination of the solubility is difficult, due to hydrolysis taking place in the presence of the acid. However, a number of determinations of the solubility showed that the solubility does decrease as the acid concentration increases up to a concentration of 0.3 M. and this decrease is of the same order of magnitude as the increase in $\frac{(k_1'F_e)}{a_H \cdot a_w}$. Another factor to be considered is the possibility of a change in the hydrogen ion activity of the acid caused by the presence of the ester. An attempt was made by the electromotive force method to determine this change, but owing to difficulties caused by complex liquid junction potentials, little reliance can be placed on the results, and further work must be done before any conclusions may be drawn.

In conclusion it is thought that the minimum in the velocity constant—log c plot is contributory evidence of the theory of the independent activity coefficients as developed by Mac Innes and Harned. On the other hand it is thought that further evidence has been obtained for the activity theory of homogeneous catalysis, and that work of this nature is in the right direction.

Summary

(1) The general theory of hydrolysis of ethyl acetate has been considered, and the activity theory has been applied.

(2) The monomolecular velocity constants of hydrolysis of ethyl acetate at different hydrochloric acid concentrations have been accurately determined at 25° C. Many determinations were made with acid concentrations in the neighborhood of 0.1 M hydrochloric acid.

(3) A solution of the general equation for the velocity constant of hydrolysis has been obtained.

(4) The velocity constants have been computed by the general equation.

(5) In four series of measurements, it has been found that the plot of the velocity constants divided by the molal concentration of the acid against log c_1 (c_1 = molal concentration of hydrochloric acid) shows a minimum at 0.07 to 0.08 M. concentration of the acid. This is similar to the plot of the individual hydrogen ion activity coefficient against log c_1 which has a minimum at 0.18 M. acid concentration.

(6) It has been shown that the velocity constant divided by the product of the activities of the hydrogen ion and water molecule does not give a constant, but has a maximum at 0.20 to 0.30 molal concentration of hydrochloric acid.

(7) A suggestion is made that the deviation from constancy is due to one or more of the following factors:

(a) That the activity coefficient F_e of the ester varies with a variation in the acid content of the solution.

(b) That the activity of the hydrogen ion is influenced by the presence of the ester.

(c) That in the more concentrated solutions of hydrochloric acid the values given to the activity coefficient of the hydrogen ion may be in error.

(8) The kinetics of hydrolysis of ethyl acetate is very complex, but it is thought evidence has been obtained to show that the method here employed is in a general way correct.